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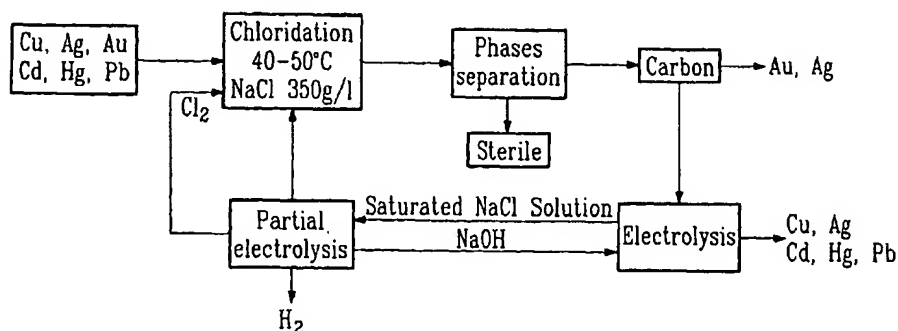
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(54) Title: METHOD FOR THE RECOVERY OF BASE AND PRECIOUS METALS BY EXTRACTIVE CHLORIDATION



(57) Abstract: A method for the recovery of base metals such as cobalt, nickel, copper, lead, zinc, mercury and cadmium, precious metals such as silver and gold, as well as the platinum group metals, comprising ruthenium, rhodium, palladium, osmium, iridium and platinum from fresh ore, mine tailings and industrial wastes by a series of steps which include analysing the ore, mine tailings or industrial wastes to determine the presence of one or more of the above mentioned metals; chloridating the ore with a strength determined by the presence of the most refractory of the metals ascertained by the analysing step, in the presence of a source of chloride ions in an amount determined by the metals present to form a solution of metal chlorides and a sterile residue; separating the solution of metal chlorides from the residue to produce a filtered solution of metal chlorides; recovering the metal chlorides from the filtered solution of metal chlorides to produce a barren solution; recycling the source of chloride ions. In one preferred embodiment the chloridation process is carried out with chlorine gas at temperatures ranging from 40 to 50 °C in the presence of a near saturated solution of either NaCl, KCl or CaCl₂. In a second preferred embodiment the chloridation process is carried out with chlorine gas at temperatures ranging from 500 to 600 °C in the presence of about 5 % of either solid NaCl, KCl or CaCl₂. In third preferred embodiment the chloridation procedure is carried out with concentrated hydrochloric acid at temperatures ranging about 100 °C.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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TITLE OF THE INVENTION

Method for the recovery of base and precious metals by extractive chloridation.

5 FIELD OF THE INVENTION

The present invention pertains to a method for the recovery of base metals such as cobalt, nickel, copper, lead, zinc, mercury and cadmium, precious metals such as silver and gold, as well as the platinum group metals, comprising ruthenium, rhodium, palladium, osmium, iridium and platinum,
10 from fresh ore, mine tailings and industrial wastes.

BACKGROUND OF THE INVENTION

Base metals, precious metals and the platinum group metals (PGM), are used in a broad spectrum of industrial applications. Their extraction or recovery is
15 therefore of major importance.

It is quite frequent to find several of these base or precious metals, in a specific ore body. For example, gold is often found in variable amounts in association with copper or zinc. The presence of silver in some zinc or lead
20 minerals has been known since earliest mining operations. There are quite often significant amounts of chromium and/or nickel or copper associated with the PGM bearing ores. Therefore, the recovery of more than one metal in a single operation is of interest. However, with many existing extraction procedures, the presence of one metal may prevent a smooth extraction of
25 another one, as is observed in the case of gold extraction with cyanide, while in the presence of silver or copper.

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The tailings from the mining of these complex ores, especially from the old sites, may contain significant amounts of either base or precious metals. A similar situation prevails to some extent with complex industrial metallic wastes, which may contain significant amounts of the platinum group metals.

- 5 The composition of the ashes, resulting from the incineration of wastewater muds of the city of Toronto (Canada), is an example of such a complex industrial waste. The composition was shown to contain 350 g/T of silver, 4 g/T of gold, 0.64 g/T of platinum, 0.5 g/T of palladium and 0.29 % of copper. These values resemble more the numbers expected from the analysis of a
10 high quality ore, rather than a waste material.

- Because of the diversity in physical and chemical properties of base, precious metals and PGM metals, there does not exist a common procedure, allowing for the recovery of most, if not all, of these metals in a single operation. As a
15 result, a large number of methods are currently used in the recovery of these metals. Ever since the oxidation of sulfides has been abandoned for environmental reasons, metals such as nickel and cobalt are leached by agent, taking advantage of their propensity to complexation. Gold is generally collected through cyanide extraction. Lead and zinc sulfides continue to be
20 roasted, wherein the liberated SO₂ is being used in the manufacturing of sulfuric acid. The same situation applies to mercury. Copper is either obtained by heap leaching with sulfuric acid or obtained through smelting and electro-refining. Finally, the PGM are obtained through a very complex series of pyrometallurgical processes, involving the associated metals comprising
25 copper, nickel, cobalt and chromium. These methods are generally quite specific, being useful only in the recovery of at most one or a few of the metals in one basic operation.

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OBJECT AND STATEMENT OF THE INVENTION

It is an object of the present invention to provide a method for the recovery of base metals (Co, Ni, Cu, Zn, Cd, Pb, Hg), precious metals (Ag, Au) and platinum group metals (Ru, Rh, Pd, Os, Ir, Pt) from fresh ore, mine tailings and industrial wastes, in one type of operation. The interest for such a procedure stems from the composition of some ores, certain mine tailings and industrial wastes, where several of the above listed metals are present.

This is achieved by a method, which consists of a series of steps including:

- 5 (a) analyzing the ore, mine tailings or industrial wastes to determine the presence of one or more of the above mentioned metals;
- 10 (b) chloridating the ore with a strength determined by the presence of the most refractory of the metals ascertained by the analyzing step, in the presence of a source of chloride ions in an amount determined by the metals present, to form a solution of metal chlorides and a sterile residue;
- 15 (c) separating the solution of metal chlorides from the residue to produce a filtered solution of metal chlorides;
- (d) recovering the metal chlorides from the filtered solution of metal chlorides to produce a barren solution; and
- 20 (e) recycling the source of chloride ions.

The combination of these metals with different low-cost cations, as for example sulfates, phosphates and chlorides, leads in many instances to the formation of insoluble species. In the case of the formation of chlorides
25 however, it was observed that the corresponding solubilities are directly

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related to the ionic strength of the solutions in chloride ions. This situation is readily understood by examining the solubility of the chlorides of Cu^+ , Ag^+ , Hg_2^{2+} and Ir^{3+} . These metallic chlorides are either water insoluble or of very low water solubility. It was experimentally observed, however, that when the chloride ion concentration in the solution is raised to an appropriate level by the addition of, for example a chloride such as sodium chloride, then the solubility of the less soluble metal chlorides is substantially increased.

With the implementation of a chloridation process able to generate the corresponding chlorides of the metallic species to be reclaimed, namely base metals, precious metals and platinum group metals (commonly found in complex ores, mine tailings or industrial wastes), it will then be possible to simultaneously solubilize these chlorides if the chloride ionic strength is at the appropriate level. With this procedure, the metallic species, present either in the form of a free metal, an oxide, a silicate, a carbonate, a sulfide, an arsenosulfide or a polysulfide, will be transformed into a soluble chloride, if the ionic strength in chloride ions is at a sufficient level.

The ionic strength requirement in chloride ions, necessary to achieve solubility, will vary from metal to metal and will consequently be directly dependent on the requirements in chloride ion by the least soluble of the metal chlorides in a given mixture of metals.

It was determined that, by adjusting the conditions of the chloridation procedure and by adjusting the ionic strength of the chloride ions in solution, all base metals, precious metals (including PGM) along with mixtures of both types of metals could be reclaimed.

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Unless defined otherwise, the scientific and technological terms and nomenclature used herein have the same meaning as commonly understood by a person of ordinary skill. Generally, procedures such as recovering a-or more compounds from a reaction mixture are common methods used in the art. Such standard techniques can be found in reference manuals such as for example Gordon and Ford (The Chemist's Companion: A Handbook of Practical Data, Techniques and References, John Wiley & Sons, New York, NY, 1972).

10 The present description refers to a number of routinely used chemical terms. Nevertheless definitions of selected examples of such terms are provided for clarity and consistency.

As used herein, the terminology "recovering" a desired compound or compounds or the like, well known in the art, refers to such a desired compound or compounds or the like having been isolated from other components of a reaction mixture.

As used herein, the terminology "concentrated" well known in the art, refers to an acidic solution having a concentration equal to or higher than 15%.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

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DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram illustrating the various steps of one embodiment of the method according to the present invention;

- 5 Figure 2 is a block diagram illustrating the various steps of a second embodiment of the method according to the present invention; and

Figure 3 is a block diagram illustrating the various steps of a third embodiment of the method according to the present invention.

10

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The conditions of chloridation vary with different metals, being as low as 100°C for nickel oxide and as high as 600 °C for the platinum group metals. While doing the chloridation, it is necessary to have the source of chloride
15 ions, normally sodium chloride, present in the reaction mixture so as to have available *in situ* the chloride ion concentration required for the solubilisation at the time of leaching, upon completion of the chloridation step. Sodium chloride is used but potassium chloride or calcium chloride can also be used.

- 20 The energy required to achieve chloridation will vary with the chemical reactivity of the metal or group of metals under consideration. To maintain the energy consumption at a minimum and taking into consideration the solubility characteristics of each metal, three levels of chloridation ability have been developed.

25

Low temperature (40-50 °C) chloridation with chlorine in the presence of a near saturated solution of sodium chloride is appropriate for metals such as

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Cu, Ag, Au, Cd, Hg, and Pb, these metals showing a rather high reactivity but giving in some instances chlorides of very low solubilities. High temperature (500-600 °C) chloridation with chlorine in the presence of a source of chloride ions, such as solid NaCl, KCl or CaCl₂, (approximately 5% by weight) is
5 required mainly for PGM. Chloridation using hydrochloric acid at a temperature near 100 °C, is appropriate for base metals, particularly when iron is present.

The selection of one of these methods allows for the recovery of the metal
10 values from most combinations found either in nature or in antropogenic wastes.

In the case of chloridation with chlorine at (40-50 °C), the operation is conducted in a near saturated solution of either NaCl, KCl or CaCl₂ and the
15 precious metals are readily recovered over activated carbon, while the residual base metals are obtained by electrolysis, leaving behind a barren solution. The near saturated salt solution is then recycled for further operation.

In the case of high temperature chloridation, upon completion of the
20 chloridation step in the presence of approximately 5% by weight of solid NaCl, KCl or CaCl₂, the dry mixture is leached with concentrated hydrochloric acid (~15%) so as to extract the soluble metal chloride species from the sterile residual materials. This is followed by a filtration step in order to separate the solution of metal chlorides from the sterile residual materials. Since chlorine
25 is an oxidant, the chloridation process at 500-600 °C constitutes a strong oxidation reaction. The metal chlorides will therefore be in solution at their maximum valency. To obtain the free metals in reduced state, a variety of

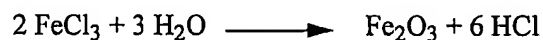
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methods are available. However, the selection of these methods must take into account the very strong dissolving power of the chloride-rich acid solution. Therefore, in order to avoid incomplete recovery or redissolution of the desired metals, the following procedure was found to be very efficient.

5

Circulating the acid solution obtained after chloridation with chlorine and leaching with concentrated HCl over a bed of activated carbon, results in the retention of all the platinum group metals and all of the gold. The base metals can be extracted by electrolysis. The remaining so-called barren solution is
10 recycled allowing for the recovery of the source of chloride ions and concentrated HCl, for further operation.

In the case of hydrochloric acid leaching, applied to a mixture of base metals, the substrate may contain substantial amounts of iron in the form of sulfides
15 (pyrites, etc...), oxides (limonites, etc...) or metallic iron. The chloridation will transform part of this iron into ferric chloride and in doing so, will consume significant amounts of chlorine. In order to recover this chlorine fixed on iron, the acid solution of ferric chloride and other metallic chlorides is evaporated and heated at temperatures of 200-250 °C while in the presence of moisture.
20 Under such conditions the ferric chloride is subjected to hydrolysis, resulting in its transformation to ferric oxide with the concomitant liberation of HCl as is shown by the following equation:

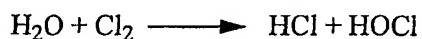


It is important to note that the remaining metal chlorides present in the
25 mixture, namely, NiCl_2 , CoCl_2 , CuCl_2 , PbCl_2 , AgCl , ZnCl_2 , HgCl_2 and CdCl_2

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are not affected by this mild hydrolysis. All of these chlorides can be separated from the ferric oxide by leaching with water. They can then be individually separated and isolated by techniques such as selective electrolysis (Cu, Ni, Co) and selective sulfide or pH adjustment precipitations, 5 techniques well known by those familiar in the art.

The recovery of metal values by either low or high temperature chloridation, results in the formation of a barren solution containing the source of chloride ion (NaCl, KCl or CaCl₂). This barren solution is acidic in nature due to the 10 presence of hydrochloric acid, resulting from the dissolution of chlorine gas according to the following equation:



In the case of low temperature chloridation, approximately 99% of the barren solution is recycled to the chloridation step whereas about 1% is subjected to 15 electrolysis. Chlorine gas is produced in the course of the electrolysis and is recycled to the chloridation step as well. Furthermore, during the electrolytic procedure, sodium hydroxide (NaOH) is generated, in equimolar amounts to chlorine gas. The sodium hydroxide is collected and used to treat the barren solution upon completion of the recovery of the metal values.

20 In the case of high temperature chloridation, approximately 99% of the barren solution is recycled to the chloridation step and wherein HCl is produced which is recycled to the lixiviation step. Approximately 1% of the barren solution is subjected to electrolysis, resulting in the production of chlorine gas that is also recycled to the chloridation step. As was previously mentioned, the 25 electrolytic procedure leads to the formation of sodium hydroxide (NaOH), in

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equimolar amounts to the generated chlorine gas. As was the case for the low temperature chloridation, the sodium hydroxide is collected and used to treat the barren solution upon completion of the recovery of the metal values.

- 5 These different operations are illustrated in Figures 1-3 of the present application.

As mentioned previously, the presence of a high chloride concentration is a basic requirement for the implementation of the invention. It has been
10 established that the chloridation of Au and Ag using chlorine gas could be carried out at low temperatures (30-50 °C) when in the presence of a near saturated solution of sodium chloride. It is noted that near saturated solutions of potassium chloride or calcium chloride are also effective. In the case of the platinoids, however, the chloridation with chlorine gas must be performed at
15 temperatures ranging from 500-600 °C while in the presence of a solid source of chloride ions, achieved by the addition of about 5% by weight of sodium chloride. It is also noted that the solid source of chloride ions can also be potassium chloride or calcium chloride, used in the same proportions. This chloridation procedure is followed by a lixiviation step using hydrochloric acid.
20 In the case of the base metals (Cu, Ni, Co, Zn, Pb, Fe), the chloridation procedure can be effected with hydrochloric acid. With both types of chloridation (Cl_2 or HCl), the main group metals (Cd, Hg, Pb) will be lixiviated when in the presence of a strong chloride concentration such as for example a near saturated sodium chloride solution.

25

The operation of the system calls for a closed circuit approach, more specifically:

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1. The near saturated solution of NaCl, KCl or CaCl_2 in the low temperature chloridation procedure, is recycled to the system after removal of the leached metal values by activated carbon (Au, Ag) and electrolysis (Cu, Ag, Cd, Hg, Pb).
- 5 2. The high temperature chloridation gives a leach in concentrated hydrochloric acid. The hydrochloric acid is recycled after removal of the metal values (mainly the platinum group metals) by electrolysis, by activated carbon or by specific ion exchange resins under acidic conditions.
- 10 3. The hydrochloric acid used in the chloridation of the base metals is recycled by the mild thermal treatment of ferric chloride.

The chloridation process while in the presence of a high concentration of chloride ions, offers flexible avenues to the low cost extraction of a wide
15 variety of metals, such as base metals, platinum group metals and precious metals. The strength of the reagents (Cl_2 or HCl) and the operating temperatures (40-50 °C or 500-600 °C) are adaptable to the sample at hand and hence the combination of metals to be recovered.

20

EXAMPLES

EXAMPLE 1

- 25 Recovery of the metallic values present in the ashes resulting from the incineration of wastewater sludges.

Municipal wastewaters carry significant amounts of organic matter in suspension. These waters are therefore first flocculated and filtered before

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treatment. Accordingly, the city of Toronto (Canada), uses ferrous chloride as a flocculating agent in the treatment of its wastewaters. The solid obtained after filtration is incinerated, so as to reduce its volume and eliminate bio-toxic elements. The resulting ashes revealed the following composition: Au: 4.01 g/T; Ag: 5.05 g/T; Pt: 0.64 g/T; Pd: 0.51 g/T; Fe: 21.7%; Cu: 0.29%; Zn: 0.23%; Ni: 0.011%. Monthly samples of this material displayed maximum variations of $\pm 5\%$ over a 1-year period. This material was submitted to high temperature chloridation.

- 5
- 10 A 50.0 g sample of ashes was placed in a tubing, known under the trademark Vycor, after being well mixed with a 4.0 g sample of sodium chloride. The sample was then heated in an electric furnace for 4 hours at a temperature of 575 °C. During this heat treatment, a slow stream of nitrogen (20 ml/min), charged with chlorine gas, was circulated through the Vycor tube. The
- 15 chlorine gas was generated *via* the electrolysis of a solution of sodium chloride (35.0 g) in 15 % HCl (250 ml). The nitrogen stream first vented the anodic compartment before reaching the reaction tube (current of 5.0 amp, 4.5 volts, anode of graphite). Approximately 0.35 moles of chlorine gas were produced. After contacting the sample with the so produced chlorine gas, the
- 20 sample was cooled and extracted with 15% HCl (150 ml) and heated to approximately 100 °C for one hour. The reaction mixture was then filtered, to produce an acidic solution of metal chlorides and a residue. The solid residue, while wet, was taken up with a saturated NaCl solution (200 ml) and heated at 100 °C for one hour and filtered and rinsed with two 20 ml portions of a
- 25 saturated NaCl solution. The acid solution and the salt solution were then analyzed for their metal content. The ashes were analyzed for any residual metal values. The acid solution was revealed to contain 97% of the gold, 12%

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of the silver, 98% of the platinum, 99% of the palladium, 12% of the iron, 96% of the copper, 85% of the zinc and 92% of the nickel present in the initial ashes. The sodium chloride rinsings contained 84% of the initial amount of silver. Contacting the acid solution with activated carbon (25 g; Norit A) 5 resulted in the removal of Au, Pt and Pd below detectable level (0.001 ppm). After removal of the precious metals by activated carbon, the acidic solution was evaporated to dryness and the resulting solid heated up to 250 °C. The hydrochloric acid produced in the heating process was collected and recycled. The residual solid was rinsed with water and the extracted base metals (in the 10 present example copper chloride) collected as sulfides.

EXAMPLE 2

15 Recovery of gold, silver and mercury

A 50 g sample of mine tailings from the Pedernalillo mine in the Province of Zacateca (Mexico), containing Au: 2.4 g/T; Ag: 91.1 g/T and Hg: 0.7 g/T, was suspended while stirring in a solution of sodium chloride (170 g) in water (500 ml). The suspension was maintained with a mechanical stirrer and saturated 20 with chlorine gas. The temperature was maintained with a water bath kept at 40 °C. After chloridating for two hours, the suspension was filtered and the solid residue rinsed with two 20 ml portions of a saturated NaCl solution. The combined filtrate and rinsings were then contacted with activated carbon (10 g) over a period of one hour and the carbon filtered and dried. A subsequent 25 analysis of the carbon and residual solution indicated that 96% of the gold and 75% of the silver initially present in the tailings were collected on the carbon. The residual solution was submitted to electrolysis (2.0 V, 1.0 amp.) using a

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copper cathode. After 15 minutes, all of the mercury and all of the residual silver were deposited on the cathode.

EXAMPLE 3

5

Recovery of silver and lead.

A 50 g sample of ore from the Pachuca mine, located in the Province of Hidalgo (Mexico) containing Pb: 0.9% and Ag 42 g/T was treated in a manner
10 similar to Example 2. The suspension, after chloridating for 2 hours at 40 °C, was filtered, rinsed and submitted to electrolysis. 99% of the initial Pb and 96% of the initial Ag were collected on a copper cathode. At the graphite anode, the evolution of chlorine gas was noted, which was subsequently recycled for further reaction, as was the solution deprived of Ag and Pb.

15

Although the invention has been described above with respect to three specific embodiments, it will be evident to a person skilled in the art that it may be modified and refined in various ways. It is therefore wished to have it understood that the present invention should not be limited in scope, except
20 by the terms of the following claims.

25

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CLAIMS

1. A method for the extraction from fresh ore, mine tailings or industrial wastes of metals selected from the group consisting of: cobalt,
5 nickel, copper, lead, zinc, mercury, cadmium, silver, gold, ruthenium, rhodium, palladium, osmium, iridium and platinum, said process comprising the steps of:
 - (a) analyzing said ore, mine tailings or industrial wastes to determine the presence of one or more of said metals;
 - 10 (b) chloridating said ore with a strength determined by the presence of the most refractory of said one or more metals, ascertained by said analyzing step, in the presence of a source of chloride ions in an amount determined by said one or more metals, to form a solution of metal chlorides and a sterile residue;
 - 15 (c) separating said solution of metal chlorides from said residue to produce a filtered solution of metal chlorides;
 - (d) recovering said metal chlorides from said filtered solution of metal chlorides to produce a barren solution; and
 - (e) recycling said source of chloride ions.
- 20 2. A method as defined in claim 1 wherein, when said analyzing step reveals the presence of metals selected from the group consisting of: copper, cadmium, mercury, lead, silver and gold, said chloridating step is carried out in the presence of said source of chloride ions with chlorine gas at temperatures ranging from 40 to 50 °C producing said
25 solution of metal chlorides and said sterile residue.

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3. A method as defined in claim 2, wherein said source of chloride ions is a near saturated solution of a soluble chloride, selected from the group consisting of NaCl, KCl and CaCl_2 .

4. A method as defined in claim 3, wherein said sterile
5 residue is removed from said solution of metal chlorides by filtration, producing a first filtered solution of metal chlorides and a filtered sterile residue.

5. A method as defined in claim 4, wherein said filtered
sterile residue is washed with a saturated chloride solution to generate, after
10 a second filtration step, an extracted sterile residue and a second solution of metal chlorides.

6. A method as defined in claim 5, wherein said saturated chloride solution is composed of a soluble chloride, selected from the group consisting of NaCl, KCl and CaCl_2 .

7. A method as defined in claim 6, wherein said first
15 solution and said second solution of metal chlorides are mixed to produce a combined solution of metal chlorides.

8. A method as defined in claim 7, wherein said combined
solution of metal chlorides is contacted with activated carbon to remove the
20 chlorides of gold and silver, resulting in the formation of a left-over solution of remaining metal chlorides.

9. A method as defined in claim 8, wherein said left-over
solution of remaining metal chlorides is electrolyzed, to selectively recover the
remaining metals, producing said barren solution and said remaining metals.

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10. A method as defined in claim 9, wherein said remaining metals comprise copper, cadmium, mercury and lead and wherein said barren solution is recycled, to recover said source of chloride ions.

11. A method as defined in claim 10, wherein about 99% of
5 said barren solution, comprising said source of chloride ions, is recycled to said chloridating step and wherein about 1% of said barren solution is subjected to electrolysis to produce said chlorine gas which is recycled to said chloridating step and wherein said electrolysis also results in the formation of NaOH.

12. A method as defined in claim 11, wherein said NaOH is
10 produced in equimolar amounts to said chlorine gas, and wherein said NaOH is used to treat said barren solution upon completion of said recovery of said metal values.

13. A method as defined in claim 1 wherein, when said
15 analyzing step reveals the presence of metals selected from the group consisting of: ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, mercury and lead, said chloridating step is carried out in the presence of said source of chloride ions with chlorine gas at temperatures ranging from 500 to 600 °C producing a dry mixture composed of said metal chlorides and said
20 sterile residue.

14. A method as defined in claim 13, wherein said source of chloride ions is about 5% by weight of a solid selected from the group of NaCl, KCl and CaCl₂.

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15. A method as defined in claim 14, wherein said dry mixture is lixiviated with concentrated hydrochloric acid, producing a lixiviated solution of metal chlorides and said sterile residue.

5 16. A method as defined in claim 15, wherein said lixiviated solution of metal chlorides is filtered, producing a filtered solution of metal chlorides and a filtered sterile residue.

10 17. A method as defined in claim 16, wherein said filtered solution of metal chlorides is contacted with activated carbon to remove the chlorides of ruthenium, rhodium, palladium, osmium, iridium, platinum, and gold from said solution of metal chlorides, resulting in the formation of a left over solution of remaining metal chlorides.

15 18. A method as defined in claim 17, wherein the remaining metals are recovered from said left over solution of remaining metal chlorides by a process selected from the group of processes consisting of electrolysis, solvent extraction, specific ion-exchange resins and pH adjustment precipitation, producing said barren solution and said remaining metals.

19. A method as defined in claim 18, wherein said remaining metals comprise mercury and lead and wherein said barren solution is recycled, to recover said source of chloride ions.

20 20. A method as defined, in claim 19, wherein about 99% of said barren solution, comprising said source of chloride ions is recycled to said chloridating step and wherein hydrochloric acid is produced which is recycled to said lixiviation step and wherein about 1% of said barren solution is subjected to electrolysis to produce said chlorine gas which is recycled to
25 said chloridating step and wherein said electrolysis also results in the

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formation of NaOH.

21. A method as defined in claim 20, wherein said NaOH is produced in equimolar amounts to said chlorine gas, and wherein said NaOH is used to treat said barren solution upon completion of said recovery of said metal values.

22. A method as defined in claim 1 wherein, when said analyzing step reveals the presence of metals selected from the group consisting of: copper, cobalt, nickel, zinc, lead and iron, said chloridation step is carried out with concentrated hydrochloric acid at temperatures of about 100 °C producing said solution of metal chlorides and said sterile residue.

23. A method as defined in claim 22, wherein said solution of metal chlorides and said sterile residue is evaporated and heated at temperatures ranging from 200 to 250 °C in the presence of moisture, to selectively transform ferric chloride into ferric oxide, producing a solid residue composed of remaining metal chlorides, ferric oxide and said sterile residue and wherein hydrochloric acid is produced which is recycled to said chloridating step

24. A method as defined in claim 23, wherein said solid residue is leached with water resulting in the formation of a solution of said remaining metal chlorides and a second solid composed of said ferric oxide and said sterile residue.

25. A method as defined in claim 24, wherein said solution of said remaining metal chlorides is filtered, producing a filtered solution of said remaining metal chlorides and a filtrate composed of said second solid.

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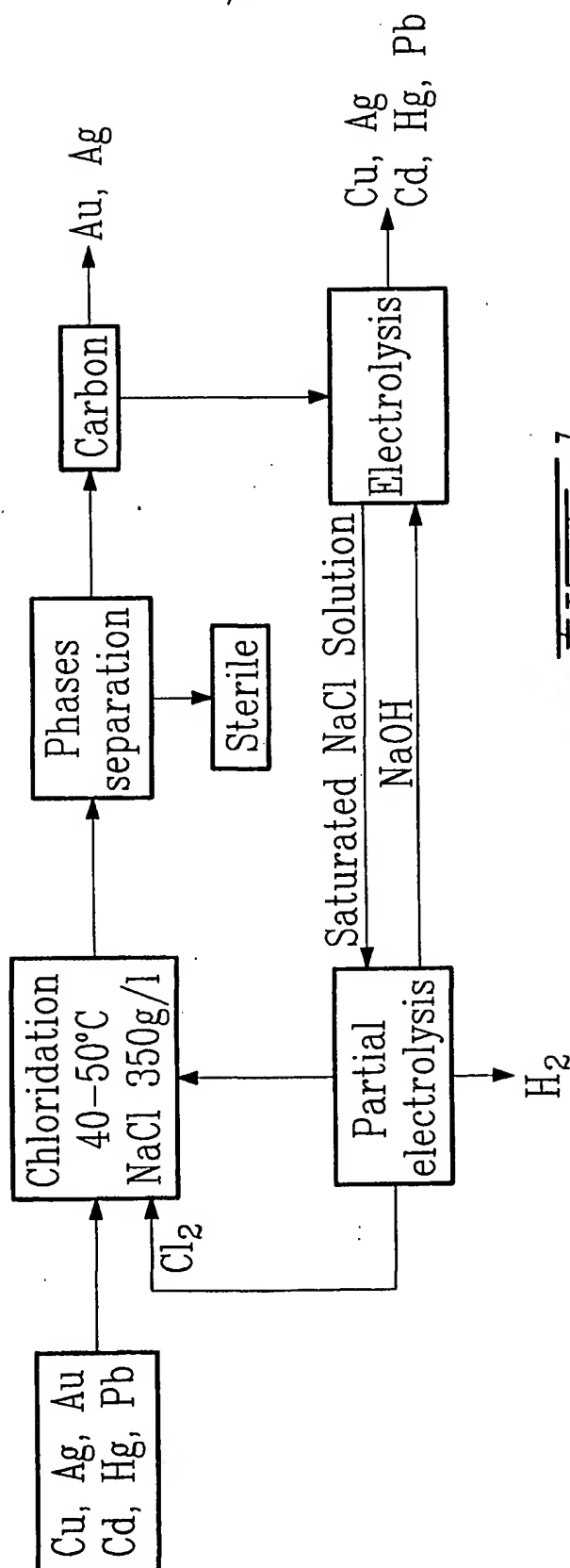
26. A method as defined in claim 25, wherein the remaining metals are recovered from said filtered solution of said remaining metal chlorides, by a process selected from the group of processes consisting of electrolysis, solvent extraction, specific ion-exchange resins and pH
5 adjustment precipitation, producing said barren solution and said remaining metals.

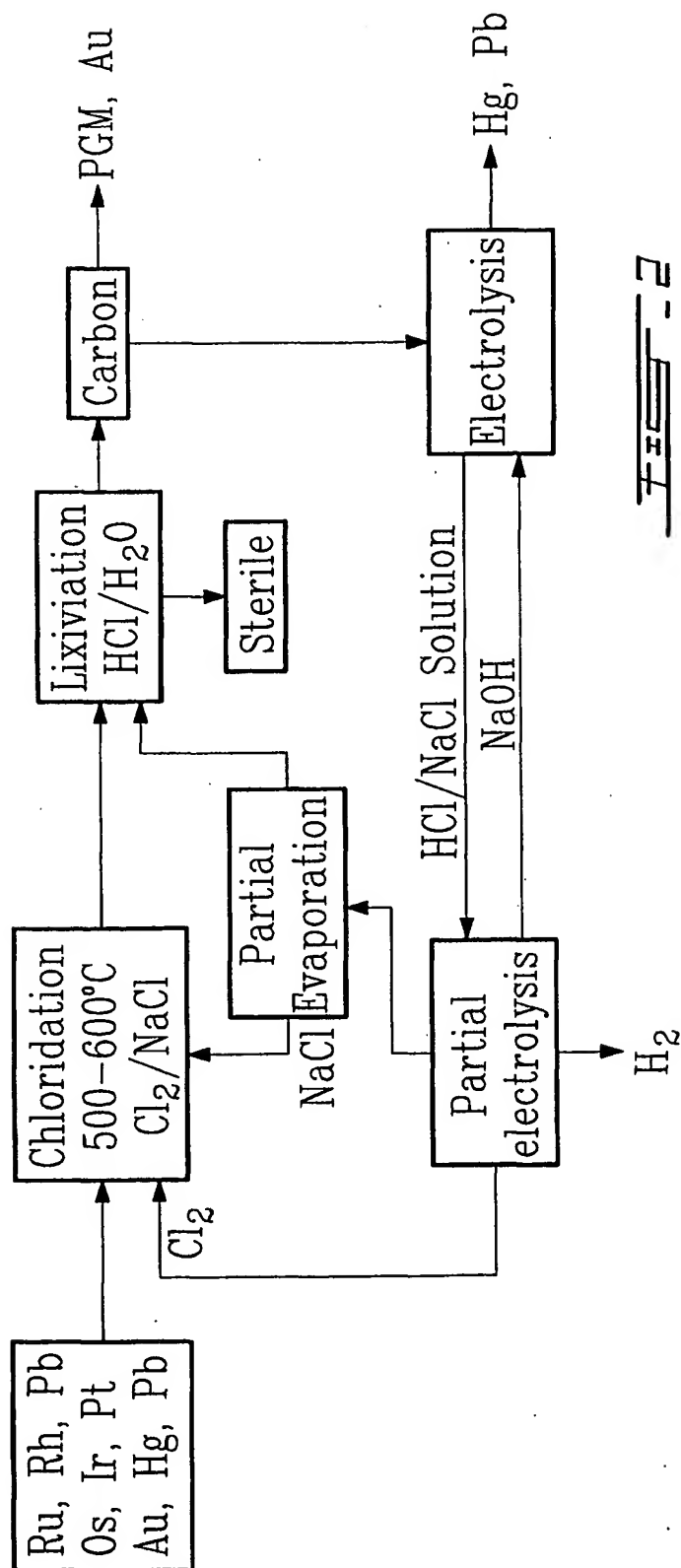
27. A method as defined in claim 26, wherein said remaining metals comprise copper, cobalt, nickel, zinc, or lead.

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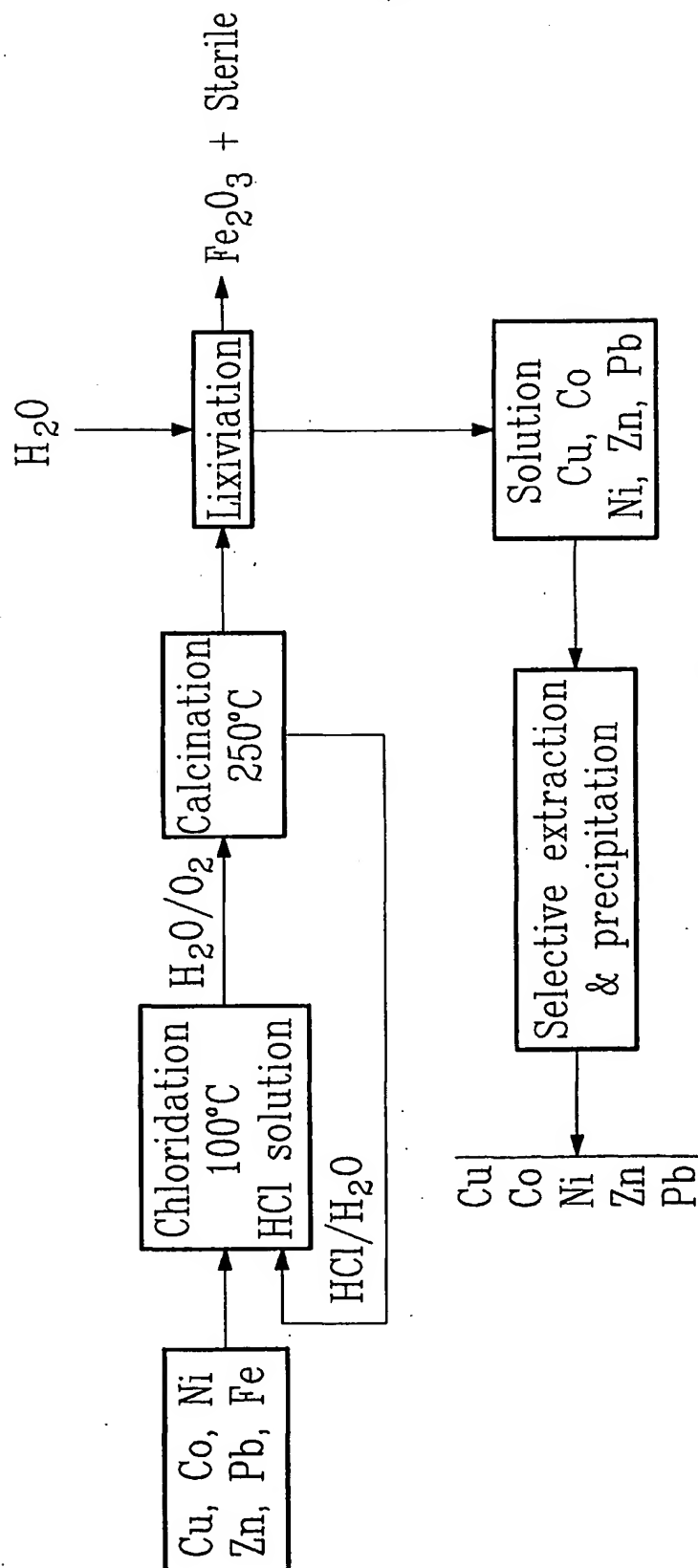
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FIG. 1



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FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No

PC., CA 00/01590

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B1/08 C22B11/06 C22B3/10 C22B7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 1 228 989 A (DUOMETAL 1984 INC) 10 November 1987 (1987-11-10)	1
Y	page 5, line 7 - page 7, line 15; claims 1-6,8,10,12; examples 16-27	2-12
X	GB 452 832 A (HENRI BUTTGEBACH;MINES REUNIES) 31 August 1936 (1936-08-31)	1
Y	page 1, line 44 - line 82 page 2, line 22 - line 70	2-12
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"G" document member of the same patent family

Date of the actual completion of the international search

23 August 2001

Date of mailing of the international search report

22. 11. 01

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 00/01590

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	VINALS J ET AL: "LEACHING OF GOLD, SILVER AND LEAD FROM PLUMBOJAROSITE-CONTAINING HEMATITE TAILINGS IN HCL-CACL2 MEDIA" HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 26, no. 2, 1 March 1991 (1991-03-01), pages 179-199, XP000201577 ISSN: 0304-386X the whole document ---	2-12
Y	US 4 723 998 A (O'NEIL GREGORY R) 9 February 1988 (1988-02-09) column 4, line 42 -column 5, line 16 -----	2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

page 2 of 2

INTERNATIONAL SEARCH REPORT

national application No.
PCT/CA 00/01590

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-12

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-12

A method for the extraction of metals selected from Co, Ni, Cu, Pb, Zn, Hg, Ag, Au, Ru, Rh, Pd, Os, Ir and Pt from ore, mine tailings or industrial wastes by chloridating said material with chlorine gas in the presence of a source of chloride ions (NaCl, CaCl₂, KCl) to form a solution of metal chlorides and a sterile residue, recovering said metal chlorides from said solution - after its separation from said residue by filtration - to produce a barren solution, and recycling said source of chloride ions (Figure 1).

2. Claims: 13-21

A method of extracting metals selected from Ru, Rh, Pd, Os, Ir, Pt, Au, Hg and Pb from ore, tailings or industrial waste by chloridating the same with chlorine gas at temperatures from 500 to 600 C in the presence of a source of chloride ions, thereby producing a dry mixture composed of chlorides of said metals and a sterile residue (Figure 2).

3. Claims: 22-27

A method for the extraction of metals selected from copper, cobalt, nickel, zinc, lead and iron from ore, mine tailings or industrial wastes by a chloridation step performed with concentrated hydrochloric acid at temperatures of about 100 C so as to produce a solution of metal chlorides and a sterile residue (Figure 3).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 00/01590

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CA 1228989	A	10-11-1987	CA 1228989 A1	10-11-1987
GB 452832	A	31-08-1936	NONE	
US 4723998	A	09-02-1988	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)